PATENT SPECIFICATION

NO DRAWINGS

1,044,205

1,044,205

Date of Application and filing Complete Specification: July 31, 1963.
No. 30297/63.
Application made in Germany (No. B68299 IVd/39c) on Aug. 3, 1962.
Complete Specification Published: Sept. 28, 1966.

The inventors of this invention in the sense of being the devisers thereof within the meaning of Section 16 of the Patents Act 1949 are:- Erwin Ritter and Wilhelm Mueller, citizens of the Federal Republic of Germany, residing respectively, at 18 Beethovenstrasse, Schifferstadt/Pfalz; and 61 Diakonissenstrasse, Speyer/Rhein; both Federal Republic of Germany;

Index at acceptance:—B5 A(1R14C1A, 1R14D, 1R15, 1R29X)

Int. Cl.:—B 29 d, f

COMPLETE SPECIFICATION

Production of Polyamide Shaped Articles

We, BADISCHE ANILIN- & SODA-FABRIK AKTIENGESELLSCHAFT, a German Joint Stock Company of Ludwigshafen/Rhein, Federal Republic of Germany, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the production of polyamide molded articles in rotating molds.

It is known to prepare molded articles, such as pipes and gears, from molten polyamides by centrifugal casting. For this purpose the polyamides must be heated to temperatures at which, especially in the presence of oxygen, they are somewhat degraded and this becomes evident in a worsening in the mechanical properties and by discoloration. It is therefore necessary to carry out this process under a protective gas, such as nitrogen or carbon dioxide. For this purpose, particularly when making molded articles having large dimensions, it is necessary to have complicated and expensive apparatus.

It is also known to prepare polyamide molded articles using a mixture of melts of lactams having seven or more ring members, activators and catalysts and if desired additives (such a mixture hereinafter being referred to as polymerization formulation) which is introduced into rotating molds whose rotational speed corresponds to a centrifugal acceleration which is greater than the acceleration due to gravity. In this way the melts are forced uniformly against the walls of the molds. In these rotating molds, the lactams are polymerized at temperatures between their melting points and the melting points of the polyamides so that the desired molded articles are formed. The process is known as centrifugal polymerization casting.

It is an object of the present invention to prepare by the use of rotating molds, polyamide molded articles which can be removed readily from the molds. A further object of the invention is the production of multilayer polyamide molded articles, i.e. shaped articles in which the layers consist of different polylactams, without practically any radial mixing of the layers taking place. It is another object of the invention to prepare polyamide molded articles the external surface of which corresponds to the internal surface of the mold.

Yet another object of the invention is the uniform distribution of fillers in the molded articles in cases where fillers are used.

We have found an advantageous process for the production of polyamide molded articles by polymerization of molten polymerization formulations consisting of mixtures of lactams having seven to fourteen ring members, alkaline catalysts and activators in rotating heated molds. The characteristic feature of this process is that the rotational speed of the molds corresponds to a centrifugal acceleration at every point in the interior of the molds which is less than the acceleration due to gravity (which is equal to 9.81 $m.sec^{-2}$). The preferred range is 9.7 $m.sec^{-2}$ to 0.5 $m.sec^{-2}$. In this way the melt of the polymerization formulation is not forced uniformly against the walls of the mold, but forms a pool in the lower portion of the mold which is carried up by the rotating mold to an extent which increases

as the internal friction of the melt increases as the polymerization proceeds.

Lactams having seven to fourteen ring members which are suitable for the process are for example caprolactam, oenanthlactam, capryllactam, capric lactam, laurolactam or C-substituted derivatives of these lactams, such as 3-methylcaprolactam and 4-isopropylcaprolactam. Obviously mixtures of these lactams may also be used. The lactams may additionally contains lactams connected together by a bridge member, for example methylene-bis-caprolactams.

Suitable polymerization catalysts for the process according to this invention are alkali metal, alkaline earth metal and Grignard catalysts such as metals of Groups IA and IIA of the Periodic System as shown on page 394 of "Handbook of Chemistry and Physics", 38th edition, Cleveland, Ohio, 1956—1957, for example sodium, potassium, lithium, the hydrides, oxides, hydroxides and amides of these metals, sodium or potassium compounds of alcohols, for example methanol, ethanol, butanol, lauryl alcohol, cetyl alcohol and stearyl alcohol, and Grignard reagents. Reaction products of lactams with alkali metals and alkaline earth metals and their alkaline reacting compounds, such as are described in British Patent Specification No. 868,808, are particularly suitable. These catalysts may be added to and uniformly distributed by conventional methods in the lactam melts prior to introduction into the rotatable molds, in amounts of 0.01 to 5, preferably 0.1 to 2% by weight with reference to the total weight of lactam used. It is also possible, however, to mix the catalyst with the appropriate amount of activator and lactam in the mold.

Examples of suitable activators are derivatives of inorganic and organic acids, such as halides, anhydrides, esters and nitriles, for example acetyl chloride, benzoyl bromide, terephthaloyl chloride, phthalic anhydride, succinic anhydride, triphenyl phosphate or butyl stearate, and also isocyanates and carbodiimides. Urea derivatives are particularly suitable, such as pyrrolidone-N-(carboxylic acid) - hexamethylene - diamide - 1,6, triphenylmethane - 4,4',4'' - triscarbamidocaprolactam; N-substituted carbamic esters, such as N-phenylcarbamic acid ethyl ester, and also bis-isoalkylurethanes, such as N,N'-hexamethylene - 1,6 - isopropylurethane; and also N-cyanolactams, such as N-cyanocaprolactam, N-cyanocapryllactam, and N-cyanocapric lactam. These N-cyano compounds may be prepared in known manner for example from the alkali lactamates and cyanogen chloride.

The activators may be added in amounts of 0.05 to 10, preferably from 0.4 to 5% by weight with reference to the total amount of lactam used for the polymerization. Amounts outside these limits may also be used for special purposes. The polymerization formulation is advantageously prepared by adding catalysts to the lactam melts and then, prior to pouring or spraying the melts into the rotatable molds, adding one or more of the said activators and uniformly distributing them in the melts. It is also possible, however, to add the catalyst to one portion of the melt of lactam and to add the activator to the other portion of the melt and then to mix the two melts during introduction into a rotatable mold, for example through mixing nozzles.

The conventional additives may serve as reinforcements, fillers, lubricants, delustering agents, stabilizers and the like. Suitable fillers are inorganic and organic substances, for example metal powder, such as aluminum powder or copper powder, quartz powder, ground shale, sand, diatomaceous earth, polyamides and other plastics. Examples of reinforcing agents are glass staple fibers, nonwoven glass fabrics or woven glass fabrics and other fibers and fabrics. Examples of delustering agents are titanium dioxide and zinc oxide and examples of suitable lubricants are graphite, lead powder and molybdenum sulfide.

Examples of suitable branching and crosslinking agents are alkylene, arylene and/or aralkylene diisocyanates or biscarbamidolactams, for example hexamethylene diisocyanate, toluylene diisocyanate, methylene biscaprolactams, hexamethylene biscarbamidocaprolactam, and also known trifunctional or higher functional compounds which may act at the same time as activators, such as triphenylmethane-4,4',4''-triscarbamidocaprolactam.

Molds capable of being heated and axially symmetrical with respect to at least one axis are suitable as rotatable molds. Generally the molds are heated to temperatures between 80° and 200°C prior to the introduction of the polymerization formulation in order to keep the monomer content at the outer surface of the polyamide molded article as low as possible. Polymerization may however be carried out in unheated molds if the monomer content is not important, for example when the molded articles are to be machined. The rotational speed of the mold necessary for the process according to this invention—which is hereinafter referred to as the rolling casting process—depends on the size of the molds and is sufficiently high to ensure that the centrifugal acceleration a_r of the molten polymerization formulation is less than the acceleration due to gravity g. The formula for the centrifugal acceleration is:

$$a_r = 4\pi 2 \times n^2 \times r$$

In the above equation, n is the number of revolutions per second and r is the distance of the wall from the center of the mold.

Polyamide molded articles having an external surface corresponding to the inner surface of the mold are obtained in a single

operation by the rolling casting process according to this invention, starting from monomeric lactams. It is a particular advantage that the molded articles thus prepared can be removed from the mold more readily than molded articles prepared by the centrifugal casting method. A further advantage of this new process is that multilayer molded articles can be prepared by introducing a plurality of polymerization formulations having different components successively into rotating molds. Practically no radial mixing of the layers takes place. The pouring in of the layers of the polymerization formulations may be carried out by pouring in the next layer after the preceding one has become solid. In this way, for example, tubes or rollers may be prepared which have a very low internal stress. Moreover the rolling casting process, as distinct from centrifugal casting, affords a uniform radial distribution of any fillers used. Because of the smaller centrifugal acceleration, the polymerisation contraction in a radial direction can be better accomplished by rolling casting than by centrifugal casting, whereby a better removal from the mould is obtained.

Molded articles prepared by the process according to this invention are practically free from bubbles. The monomer content is in general less than 3% by weight. The polyamides, depending on the type of initial components used, have K-values between 60 and 150, measured according to Fikentscher, Cellulose-Chemie, *13*, (1932), page 58. If crosslinking or branching agents have been added, the K-value cannot be determined, because the products obtained cannot be brought into solution. Such molded articles are distinguished by particularly high grade properties.

The invention is further illustrated by the following Examples in which the parts are by weight.

EXAMPLE 1

An aluminum tube having an internal diameter of 10 cm and a length of 49 cm and flanged at both ends is preheated to 140°C and rotated in a rolling frame at 50 r.p.m. Caprolactam (402 parts) is melted in a vessel and heated to 110°C. Then 98 parts of a reaction product of 1.3 moles of sodium methylate with 8.6 moles of caprolactam is dissolved therein. 20 parts of bis-caprolactam-N - carboxylic acid - hexamethylenediamide - 1,6 is dissolved at 100°C in a second melt of 455 parts of caprolactam and 25 parts of capryllactam. The two melts are then mixed at 100°C and poured through a concentric opening into the rotating aluminum tube. During the first ten minutes, the aluminum tube is heated externally with a gas flame and after another ten minutes the product is removed from the aluminum tube. A polyamide tube is obtained having a very glossy smooth inner and outer surface.

EXAMPLE 2

A mixture at 100°C of two melts, the first consisting of 241 parts of caprolactam and 49 parts of a reaction product of 1.3 moles of sodium methylate with 8.6 moles of caprolactam and the second consisting of 273 parts of caprolactam, 15 parts of capryllactam and 12 parts of bis-caprolactam-N-carboxylic acid-hexamethylenediamide-1,6, is introduced into the tube preheated to 140°C described in Example 1. The tube rotates at 100 r.p.m. Four minutes later, a second mixture is added composed like the first but containing additionally 30 parts of molybdenum disulfide. After a further ten minutes heating is discontinued and ten minutes after that the product is removed from the aluminum tube. When the polyamide tube obtained is cut through it may be seen that there are two layers superposed concentrically. The inner and outer surfaces of the polyamide tube are completely smooth.

EXAMPLE 3

A cylindrical mold 1 meter in length and 50 cm in internal diameter which is steam heated through central stuffing boxes is provided with removable closures, one of which has an eccentric closable opening. The mold is rotated at 35 r.p.m. and heated to 130°C. Two melts at 110°C are supplied to the mold through a mixing nozzle. One melt consists of 235 parts of caprolactam and 15 parts of a reaction product of 1.3 moles of sodium methylate with 8.6 moles of caprolactam, and the other melt consists of 228 parts of caprolactum, 10 parts of capryllactam and 13 parts of bis-(caprolactam - N - carboxylic acid) - hexamethylenediamide-1,6. Heating is discontinued after fifteen minutes and the polyamide tube obtained is removed from the mold thirty minutes later. It has a smooth inner surface and is completely homogeneous.

EXAMPLE 4

A polyamide layer having the same composition and amount as specified in Example 1 is produced in the alumnium tube specified in Example 1 which is however rotating at 80 r.p.m. Four minutes later, a glass fabric is laid in a triple layer and the same amount of the polymerization formulation is added during further rotation of the tube. The product is removed from the tube fifteen minutes later. A tube reinforced with glass fibers and having no pockets is obtained which can withstand particularly high compressive stresses.

WHAT WE CLAIM IS:—

1. A process for the production of polyamide molded articles by polymerization of molten polymerization formulations of lactams having seven to fourteen ring members, alkaline catalysts and activators in rotating heated molds, wherein the speed of rotation of the

mold corresponds at every point in the interior of the mold to a centrifugal acceleration which is less than the acceleration due to gravity.

2. A process as claimed in claim 1 wherein the rotating mould is heated to a temperature between 80° and 200°C prior to the introduction of the polymerization formulation.

3. A process as claimed in claim 1 or 2 wherein a plurality of polymerization formulations of different composition are introduced successively into the mold.

4. The process for the production of polyamide molded articles substantially as described in any of the foregoing Examples.

J. Y. & G. W. JOHNSON,
Furnival House,
14—18, High Holborn,
London, W.C.1.,
Chartered Patent Agents,
Agents for the Applicants.

Leamington Spa: Printed for Her Majesty's Stationery Office by the Courier Press.—1966.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.